

APPENDIX C

DATA VALIDATION REPORTS

**USEPA/Office of Research and Development
National Risk Management Research Laboratory**

INDEPENDENT DATA VALIDATION

Independent Data Validation of
Outer Loop Landfill Baseline Data

Performed by:

Neptune and Company

Date of Review: 4/30/2002

Baseline Data: 4th Quarter 2001

Data Packages Dates:

STL-Buffalo 12/12/2001

STL-Los Angeles 1/4/2002

NCSU Sample Collection Dates: 6/6/2000-6/30/2000

Waste Settlement Measurements: 7/2001, 10/2001, 1/2002

Task No: 39

EPA Task Order Manager: Ann Vega

Introduction: Baseline data collection is in progress for the Landfill Bioreactor Studies at the Outer Loop Landfill, Louisville, Kentucky. These activities are guided by the Quality Assurance Project Plan, latest revision (Draft Final) dated September 21, 2001. The purpose of this task is to review and validate the data obtained in this project. To accomplish this, data were obtained from Roger Green, Waste Management Incorporated. The data packages included results from Severn Trent Services (STL Buffalo) for leachate sampling performed on November 15, 2001. This report included analysis for Volatile Organic Acids that was subcontracted to Microbial Insights; Severn Trent Services (STL Los Angeles) for gas sampling performed on December 19, 2001; electronic data for MSW analysis (NCSU), and settlement data (WMI). The data represent at least one full set of quarterly results (see QAPP Section 3.0 for sampling schedule). This validation process reviewed all critical and non-critical analyses included in the data packages and outlined in the QAPP Section 3.2, tables 3-4 to 3-6. The results of the data validation are outlined below and categorized by Medium and Laboratory/Analyst data package.

Data packages were evaluated (where appropriate) for Sample Identification (QAPP Section 4.7.1), Chain of Custody (QAPP Section 4.7.3), Correct Analytical Methods (QAPP Table 5.1), Container Preservation and Holding Times (Table 4-1), Detection/Reporting Limits (QAPP Table 6-9) and Laboratory Quality Control for Critical Measurements, QAPP Section 6.4 (Tables 6-2 to 6-9).

Due to the limited amount of QC information provided in the standard (e.g. Level II) data packages, STL-Buffalo, STL-Los Angeles, and Microbial Insights were contacted to obtain raw data for the critical measurements. Data were obtained from all three laboratories and the validation results are included. Additional raw data were not requested from North Carolina State University as this laboratory had been audited, and data evaluated on April 11, 2001.

Overall the results from data validation indicate most laboratory analyses are in compliance with the QAPP quality control requirements. Findings, Observations, and Additional Technical Comments are provided in the section relevant to the issue.

Leachate Samples:

Severn Trent Services-Buffalo. Quote NY95-481. Samples Received 11/16/01. Sample Date 11/15/01. Program Manager: Amy L. Haag.

Client Sample ID	Laboratory Sample ID
51A L01	A1B44001
51B L01	A1B44002
52A L01	A1B44003
52B L01	A1B44004
73A L01	A1B44005
73B L01	A1B44006

General:

The Chain of Custody lists the bottle types but not preservative information as specified in Section 4.7.3 of the QAPP. The samples were grouped consistent with the expected preservatives (e.g. TKN, NH₃, COD, total-P were in a single container consistent with sulfuric acid preservation). The COC does not list the required BOD analysis that was performed.

OBSERVATION (1): The Chain of Custody (COC) should include the preservatives per the QAPP. BOD analysis should be included on the COC.

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Chemical Oxygen Demand (QAPP QC Activities Table 6-2): Method 410.4, STL SOP No. AWC-COD-44:

All six samples were found above the RDL (Table 6-9). But the only sample with no dilution, 73B l01, had a RL of 10 mg/L. The QAPP specified RDL is 5 mg/L. To evaluate the QC requirements specified in Table 6-2 and 6-9 (precision, accuracy) and the Lab SOP, copies of the logbooks were obtained separately from the data package. The log book shows that the QC requirements for ICV, CCV, ICB, second source standard, reactor temperature and dilutions met the requirements and reported data. It was noted that the matrix spike was not performed on the OLL samples but on one other sample from the analytical batch. Blanks on the log book are noted as "< 5", indicating that an RDL of 5 mg/L can be obtained if necessary.

OBSERVATION (2) COD reporting detection limit must be met as specified in the QAPP. Matrix spikes should be performed on OLL samples in future analyses.

Biochemical Oxygen Demand (BOD₅, QAPP QC Activities Table 6-3): Method 405.1, STL SOP No. AWC-405.1-14:

All six samples were analyzed for BOD. QAPP requirements outlined in Table 6-3 were met with the exception of sample duplicates (see Finding 1.0). The data package narrative states that samples 51A L01 and 51B I01 were initially analyzed within the holding time, however all the oxygen was depleted. These samples were re-analyzed outside of the holding times and both sets of data were reported. The reported results for these samples were reported as follows:

51A L01 (detection limit 20) 384 mg/L (flagged as an estimate)

51A L01 (detection limit 2) 221 mg/L (second analysis, out of hold, no flag on report page)

51B L01 (detection limit 20) 384 mg/L (flagged as an estimate)

51B L01 (detection limit 2) 303 mg/L (second analysis, out of hold, no flag on report page).

Review of the logbook (additional raw data requested from STL) shows that the initial analysis resulted in insufficient oxygen depletion (difference between the initial DO and final DO must be greater than 2 mg/L) for the test. This is in contrast to the data package narrative which states oxygen was depleted on the first analysis. The results of the re-analysis in triplicate (raw data, three different dilutions) varied widely:

51A L01: 87.3 mg/L, 154 mg/L, 422 mg/L, average = 221 mg/L

51B L01: 184 mg/L, 422 mg/L, average, = 303 mg/L (With the third sample the final DO value was less than 1 making the analysis invalid)

FINDING (1): Two BOD samples required re-analysis past the holding times. The missed holding times is a concern. Fortunately, in discussion with Roger Green it was learned this was not a common occurrence. The 48 hour holding time criterion means any sample that does not have a valid analysis completed at the end of the 5 day test will fail this holding time. With such variation in BOD, the laboratory is apparently meeting the holding times by setting up several sample dilutions in the first analysis. However, there is concern that the variability observed in the BOD analysis will make comparison between cells difficult. Inspection of the raw data allowed comparison of replicate samples. No “sample duplicates” at the same dilution was performed in this batch. BOD analysis on this organic rich and microbiologically active matrix can be challenging. The project participants should contact STL-Buffalo and discuss the variability in BOD results to see if improvements can be made. Sample duplicates with OLL samples needs to be performed. It may be useful to analyze these samples for CBOD₅ (nitrogenous oxygen demand inhibited) as an evaluation of this matrix effect.

Non-Critical Measurements:

Volatile Organic Compounds, Method 8260:

All six samples were analyzed for VOCs. Due to excessive foaming in the purge vessel all samples were diluted at a ratio of at least 1:10. The blank samples met the

criteria for contamination, surrogate and internal standard recoveries. Surrogate and internal standard recoveries were not reported for the test samples and therefore not reviewed. Surrogate and internal standard recoveries will be requested for data validation in future data packages.

Semi-Volatile Organic Compounds, Method 8270:

All six samples were analyzed for SVOCs. Dilution, due to the matrix effects, was performed on three of the samples. The data package narrative states, “Samples 51B L01 and 52A L01 exhibited surrogate recovery results below quality control limits for all surrogates. However, the internal standard results were compliant.” QC data containing the surrogate and internal standard results were obtained directly from STL. Surrogate recoveries for these two samples were very low (0-18%) indicating a large matrix effect (not due to dilution). This indicates results for these samples are probably biased low (in fact 52A L01 was reported as ND for all 8270 analytes).

OBSERVATION (3): Surrogate recoveries for two leachate samples analyzed by 8270 had very poor results. This indicates matrix effects, probably occurring during the extraction procedure. The potentially poor extraction could be the reason no analytes were observed in 52A L01. It is recommended that matrix spike analysis be performed on these samples to evaluate the extent of matrix effects. In general, matrix spikes should be performed on the OLL samples for all tests that are amendable, especially COD (critical measurement).

RCRA Metals, Methods 6010B, 7470 (mercury):

All six samples were analyzed for RCRA metals. The report included all metals reported as specified on bottom of QAPP Table 5.1. Potassium analyses required dilution for 51B and 52A (noted in data package narrative). However, all samples were reported with the same detection limit (5 mg/L) even though dilutions were required for some samples. Blank results were all reported as ND.

OBSERVATION (4): The Detection Limits reported for the RCRA metals are not easily derived from a comparison of samples that have different dilutions. This potential discrepancy should be clarified with STL-Buffalo.

Wet Chemistry Analysis:

Analysis	Analytical Method
Ammonia (as N)	350.1
Chloride	300.0
Electrical Conductance (Field)	120.1
Nitrite (as N)	353.2*
Nitrate (as N)	353.2
pH (Field)	150.1
Ortho Phosphate	365.2
Total Phosphate	365.2
Sulfate	300.0
Temperature (Field)	170.1
Total Dissolved Solids	160.1
Total Kjeldahl Nitrogen	351.2

The method used for nitrite analysis is 353.2. This is correct per the STL audit conducted July 18, 19, 2001. The QAPP lists method 354.1. This needs to be corrected.

ADDITIONAL TECHNICAL COMMENT (1): The QAPP needs to be modified to include the correct method (353.2) for nitrite analysis.

All six samples were analyzed for the complete suite of wet chemistry analytes. Ammonia, chloride, ortho and total phosphate, and Total Kjeldahl Nitrogen required dilutions in all samples with the exception of 73B L01 due to high concentrations.

The QAPP specified holding time for nitrite and nitrate is 48 hours. Sampling occurred from 11:35- 15:09 on 11/15/2001. Technically, all the nitrate and nitrite analysis have missed the holding time as the analysis was performed at 15:45 on 11/17/2001. The report indicates the holding time was met.

OBSERVATION (5): The holding times issue identified with nitrite/nitrate should be reviewed with STL-Buffalo.

No lab pH measurements reported.

OBSERVATION (6): STL-Buffalo is not performing pH measurement of the leachate (non-critical). Roger Green indicated that a decision was made to only do pH in the field and conductance would be done both in the field and in the laboratory. Review of the Technical System Audit report from STL-Buffalo, QAPP Modifications item #2 indicates the agreement was to perform pH both in the field and lab and only do conductance in the field. Only electrical conductance from the field is reported in the STL data package. It is reasonable to expect conductance to be more stable than pH from field to laboratory but this issue should be resolved and the QAPP modified if necessary.

Microbial Insights, Rockford TN. Point of Contact: Michael Goodrich.
Sample Date 11/15/2001, Analysis Date 11/16/2001.

Client Sample ID	Laboratory Sample ID
51A L01	A1B63901
51B L01	A1B63902
52A L01	A1B63903
52B L01	A1B63904
73A L01	A1B63905
73B L01	A1B63906

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Volatile Organic Acids, Microbial Insights, Point of Contact: Michael Goodrich. SOP No. VFA, Revision 1. (QAPP Table 6-4)

Raw QA/QC data were obtained for samples analyzed on November 15, 2001. The initial calibration data and blank met the requirements outlined in Table 6-4. The CCV and LCS samples have low recovery for Pyruvic acid (40-50% at 4 ppm). The laboratory has since started using the midpoint level (40 ppm) for CCV. The low recovery for Pyruvic acid indicates results for this analyte may be biased low, however no pyruvic acid was detected above the reporting limits found in the STL report (this work is subcontracted to Microbial Insights). However, the QAPP lists the RDL of 0.1 (Table 6-9) yet the lowest standard run is 1 mg/L. The project participants should decide if an

RDL of 1 mg/L is sufficient for the project objectives. Michael Goodrich indicated they had not performed matrix spikes this day. Michael Goodrich submitted a spreadsheet with 32 days of MS/MSD (using OLL samples) and LCS results obtained after November 15, 2001. The LCSs met the criteria (70-130% recovery) for all compounds with the exception of 12/19/2001. On this day acetic acid recovery was 69.8%. Matrix problems were indicated on several days due to spike recoveries outside the limits.

OBSERVATION (7): The project participants should decide if the reporting limits from Microbial Insights is sufficient and modify the QAPP as necessary. The QAPP (Table 6-4) requires re-analysis of spike and samples if necessary to resolve matrix problems. This should be done in future analyses to determine if the results can be improved. Microbial Insights should contact Roger Green for guidance if re-analysis results in recoveries outside the limits.

Gas Samples:

Severn Trent Services- Los Angeles. STL Lot Number M1L200214. Samples Received 12/20/2001, Date Sampled: 12/19/2001. Project Manager: Marisol Tabirara.

Client Sample ID	Laboratory Sample ID
51 G01	51 G01
52 G01	52 G01

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Fixed Gases (Carbon Dioxide, Methane, Oxygen): Method 3C (QAPP Table 6-9).

Review of the data package for Method 3C indicates the data met the QC requirements for precision and accuracy for the LCS and LCS duplicate. LCS samples had a recovery of 102 and 104% for carbon dioxide and 101 and 101 for methane. Extended raw data and sample QC data was obtained from STL-Los Angeles. Table 6-9 QA objectives for this test are listed as “To be determined.” The raw data show compliance with Method 3C requirements for initial and ongoing calibration. Sample results and RDLs are provided below for reference in determining QC objectives.

Compound	51 G01	52 G01	Reporting Limit
CO2	38%	39%	0.017%
CH4	52%	54%	0.00034%

O2	1.7%	1.1%	0.17%
N2 (not analyte per QAPP)	7.2%	4.6%	1.7%

Non-Critical Measurements:

Total Non-Methane Hydrocarbons: Method 25C Modified

The data package from Roger Green was reviewed and no QA/QC issues were found out of compliance. Method blank was ND at 30 ppm-c**. Laboratory Control Samples had 91 and 94% recovery with RPD of 2.4%. Spike amount was 3030 ppm-c. Sample results were 2100 ppm-c (51 G01) and 2300 ppm-c (52 G01) .

** ppm-c is parts per million equivalent carbon atoms. The analytical method separates each analyte, reduces the compound to CO2 which is then oxidized to CH4 and measured by a flame ionization detector. Hexane would produce six methane molecules (or carbon atoms), 1 ppm hexane is equivalent to 6 ppm-c hydrocarbon.

Hazardous Air Pollutants: Method TO-14A

The data package from Roger Green was reviewed and no QA/QC issues were found out of compliance. Method Blank was ND for all target analytes at low ppbv concentration. Laboratory Control Samples for 1,1-Dichloroethene, Methylene Chloride, Trichloroethene, Toluene and 1,1,2,2-Tetrachloroethane had recoveries of 99-109% (met limit of method) and RPD values of less than 2%.

Municipal Solid Waste Samples:

North Carolina State University. Sampling Dates: 6/6/2000 - 6/9/2000, 6/12/2000-6/15/2000, 6/20/2000-6/23/2000, 6/26/2000, 6/27/2000, 6/29/2000, 6/30/2000. Approximately 170 samples from varying depths and locations.

Roger Green provided an Excel Spreadsheet containing the results from NCSU. Approximately 170 samples (representing 26 separate horizontal sample locations) were analyzed for Organic Solids, Moisture Content, BMP, Cellulose, Lignin, and Hemicellulose. The spreadsheet contained average and RPD values.

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Organic Solids (QAPP Table 6-5):

The average Relative Percent Difference (RPD) was 2.04% well below the 25% objective. No result was above 10% RPD (maximum value was 9.6%)

Moisture Content (QAPP Table 6-6):

No replicate (precision estimates) data were found in the spreadsheet. Results from the Technical System Audit at NCSU indicated the precision objectives in Table 6-6 were unrealistic and should be removed.

Biochemical Methane Potential (QAPP Table 6-8):

The average RPD equaled 6.98%, well below the objective of 20%. Three of the 170 samples exceeded the 20% limit (29.82%, 30.34%, 41.67%). No matrix spike data were found in the spreadsheet. This should be reported for future validations.

OBSERVATION (8): NCSU should include the matrix spike results for BMP in future reports. The balance calibration records will be requested in the next data package for validation.

Non-Critical Measurements:

% Cellulose: The average RPD equaled 4.31%, only four samples (4/170) exceeded 20%.

%Lignin: The average RPD equaled 3.74%, only one sample (1/170) exceeded 20%.

%Hemicellulose: The average RPD equaled 4.52%, five samples (5/170) exceeded 20%.

Waste Management, Incorporated. GPS readings for Waste Settlement.

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Waste Settlement

Roger Green provided the settlement data in an Excel spreadsheet (monthly report). The spreadsheet contained data for July and October 2001, and January 2002. Five grid point QA/QC checks were included for each month. These grid points contain duplicate measurement of an individual location. Each location is characterized by the northing and easting coordinates carried to 1/100th. The maximum variation in replicate measurements in feet found in the data is 0.03, this corresponds to less than 1 cm. The criteria outlined in the QAPP is precision of ∇ 5cm. The data meet these precision requirements.

Waste Density (critical, field)

Measurement and calculation of waste density is based on GPS and contour information with the mass of waste put in the landfill (weight of each truck). Therefore, Waste Density measurement quality is based on the GPS data obtained for settlement and the weight calibration performed prior to truck weight measurements.

ADDITIONAL TECHNICAL COMMENT (2):Weight calibration data should be provided by WMI in the next data package.

**USEPA/Office of Research and Development
National Risk Management Research Laboratory**

INDEPENDENT DATA VALIDATION

Independent Data Validation of
Outer Loop Landfill Experimental Data

Performed by:

Neptune and Company

Date of Review: 11/27/2002

Experimental Data: 2nd - 3rd Quarters 2002

Data Packages Dates:
STL-Buffalo 10/01/2002
STL-Los Angeles 7/1/2002
STL-Los Angeles 7/23/2002

Task No: 39 TD8L
EPA Task Order Manager: Ann Vega

Introduction: Experimental data collection is in progress for the Landfill Bioreactor Studies at the Outer Loop Landfill (OLL), Louisville, Kentucky. These activities are guided by the Quality Assurance Project Plan, latest revision (Draft Final) dated July, 2002. The purpose of this task is to review and validate the data obtained in this project. To accomplish this, data were obtained from Roger Green, Waste Management Incorporated. The data packages included results from Severn Trent Services (STL Buffalo) for leachate sampling performed on September 16, 2002. This report of leachate samples included analysis for Volatile Organic Acids that was subcontracted to Microbial Insights. In addition, two data packages (STL Los Angeles) for gas analysis were received from Mr. Green. The gas sampling was performed on June 28, and June 13, 2002. No new MSW data is currently available. This validation process reviewed all critical and non-critical analyses included in the data packages and outlined in the QAPP Section 3.2, tables 3-4 to 3-6. The results of the data validation are outlined below and categorized by Matrix, importance of parameter in the project objectives and then by Analyte(s).

Data packages were evaluated (where appropriate) for Sample Identification (QAPP Section 4.7.1), Chain of Custody (QAPP Section 4.7.3), Correct Analytical Methods (QAPP Table 5.1), Container Preservation and Holding Times (QAPP Section 4.1, Table 4-1), Detection/Reporting Limits (QAPP Table 6-9) and Laboratory Quality Control for Critical Measurements, QAPP Section 6.4 (Tables 6-2 to 6-9).

Due to the limited amount of QC information provided in the standard data packages, STL-Buffalo was contacted to obtain raw data for the anions (including sulfate) and Volatile Organic (Metabolic) Acids analyses.

Overall the results from data validation indicate most laboratory analyses are in compliance with the QAPP quality control requirements. Only three Observations were noted with this report. However, as discussed in the previous data validation report, it is necessary to obtain matrix spike and/or duplicate analysis using the OLL matrix, especially for COD and BOD which are critical parameters. A discussion of reporting limits is included in the wet chemistry section. It is understood that analyzing a sample that contains high concentrations of analytes or other components can potentially compromise the integrity of an instrument. However, any steps that can be take to achieve detection status is extremely important for this project. The need to obtain results for all analytes so that each treatment cell can be compared should be emphasized to the laboratories.

Included in this report are the data for selected analytes received in this data validation project. There appears to be some evidence of differences in some of the analytes between the control cells and experimental cells, though direct comparison is not valid due to the offset in age between the cells.

Leachate Samples:

Severn Trent Services-Buffalo. Job # A02-9192, A02-9196. Samples Received 9/17/02.
Sample Date 9/16/02. Program Manager: Amy L. Haag.

Client Sample ID	Laboratory Sample ID
51A L01	A2919201
51B L01	A2919202
52A L01	A2919203
52B L01	A2919204
73A L01	A2919205
73B L01	A2919206
74A L01	A2919207
74B L01	A2919208

Table 1. Selected Analyte Results for Leachate.

Sample	Sulfate (mg/L)	BOD (mg/L)	COD (mg/L)	TDS (mg/L)	Temp. (EC)	Conductivity (UMHOS/CM)	VOA* (mg/L-C)
51A L01	120	204	2130	5800	32.9	14500	159
51B L01	41.8	97.3	1420	5020	32.9	14000	7
52A L01	32.2	106	1040	4520	34.2	8620	8
52B L01	80.6	480	1280	4260	30.0	9620	202
73A L01	127	156	675	2920	24.0	6760	0
73B L01	57.4	158	641	2640	24.1	5660	4
74A L01	100U	2340	6030	8500	33.7	15100	4328
74B L01	100U	3540	11500	10800	33.8	16600	8193

Sample	NH3 (mg/L)	TKN (mg/L)	Nitrite (mg/L)	Ortho-P (mg P/L)	Tot-P (mg P/L)	Cl- (mg/L)	K+ (mg/L)
51A L01	1170	836	0.19	3.0	4.1	1460	426
51B L01	1720	846	0.020U	6.4	17.8	1650	388
52A L01	1420	946	0.053	2.8	3.4	1110	340
52B L01	1240	438	0.020U	2.4	3.9	1010	307
73A L01	1160	371	0.078	1.4	2.5	569	237
73B L01	736	41.9	0.10	1.1	2.0	506	219
74A L01	2720	26.5	0.061	7.6	9.0	1400	533
74B L01	1420	100U	0.11	6.9	10.5	1360	565

* Volatile Organic Acids normalized on a carbon basis.

General:

The two sample coolers were received at 3EC with all samples in good condition. The Chain of Custody lists the bottle types but not preservative information as specified in Section 4.7.3 of the QAPP. The samples were grouped consistent with the expected preservatives (e.g. TKN, NH3, COD, total-P were in a single container consistent with sulfuric acid preservation) however neither preservative nor container type key is used, the numbers refer to number of bottles.

OBSERVATION (1): The Chain of Custody (COC) should include the preservatives as specified in the QAPP.

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Chemical Oxygen Demand (QAPP QC Activities Table 6-2): Method 410.4, STL SOP No. AWC-COD-44:

All eight samples were found above the RDL (Table 6-9). Samples 74A L01 and 74B L02 had very high COD concentrations (6030 and 11,500 mg/L respectively). No COD matrix spike was performed on the OLL samples, however a batch matrix spike was performed.

Biochemical Oxygen Demand (BOD₅, QAPP QC Activities Table 6-3): Method 405.1, STL SOP No. AWC-405.1-14:

All eight samples were analyzed for BOD. Samples 74A L01 and 74B L02 had very high BOD concentrations (2340 and 3540 mg/L respectively). Batch QC met the QAPP limits.

Non-Critical Measurements:

Volatile Organic Compounds, Method 8260:

All eight samples were analyzed for VOCs, the laboratory narrative indicated that no deviations from analytical protocol were encountered. The samples were diluted at a ratio of 1:10. This was done to prevent excessive foaming in the purge and trap instrument or due to high analyte concentrations. The batch blank and matrix spike samples met the criteria for surrogate and internal standard recoveries and lack of contamination. Holding times were also met.

Semi-Volatile Organic Compounds, Method 8270:

All eight samples were analyzed for SVOCs. Sample 73A L01 had one low internal standard (Perylene d-12) due to visible matrix interference (background, non-analyte compounds that produced the ion used to quantify d-12 Perylene), however no analytes were detected that use this internal standard for quantification. Sample 74B L01 had low recovery of surrogate 2-fluorophenol due to dilution. Dilution, due to the matrix effects or high analyte concentrations, was performed on seven of the samples. Holding times for extraction and analysis was achieved. Batch blanks and matrix spikes met the QAPP limits for recovery and lack of contamination.

RCRA Metals, Methods 6010B, 7470 (mercury):

All eight samples were analyzed for RCRA metals, no deviations from the protocol were encountered. Potassium analyses required dilution for all samples due to high

concentration. Preparation and analysis holding times were achieved. Batch blank and spike samples met the QAPP limits for lack of contamination and analyte recovery.

Wet Chemistry Analysis:

All eight samples were analyzed for the complete suite of wet chemistry analytes. Sample 52A L01 was originally analyzed for total dissolved solids within holding time but the result (1650 mg/L) was inconsistent with previous data. The sample was re-analyzed past the holding time but the result was in-line with previous data (4520 mg/L). Previous TDS results for this sample are provided in Table 2. Ammonia, chloride, ortho and total phosphate, and Total Kjeldahl Nitrogen (TKN) required dilutions in all samples due to matrix effects or high analyte concentrations. Sample 74B L01 was diluted by 1:1000 due to matrix effect for the TKN analysis resulting in a not detected (100 mg/L) status.

Table 2. Historical Total Dissolved Solids Results

Sample 52A L01 TDS	
Minimum:	4540
Maximum:	10400
Median:	8800
Mean:	8356
Standard Deviation:	2292

(Markwiese, et al, August 19, 2002)

The issue of high detection limits for sulfate in some samples has recently been under discussion between project participants. The exploratory data analysis report (Markwiese, et al) shows non-detect status for cells 51 and 52 at approximately 100 mg/L, previous reporting limits have been 10 mg/L. Raw data for this data package (September 16, 2002 sampling) was obtained from STL-Buffalo for the anion analytical method (300.0). Sulfate was detected in all samples above the RL of 10 mg/L with the exception of samples 74A L01 and 74B L02 which are reported as not-detected at 100 mg/L. All samples were run initially at 10% (1:10). All the sample analyses at a 10% dilution were inspected for the presence of large peaks. The chromatograms for the two samples that were reported as not detected (and therefore, not re-analyzed without dilution) do not appear significantly different from the other samples. STL-buffalo was contacted for information on why these two samples were only analyzed at 10% dilution. Amy Haag of STL-Buffalo reiterated that the matrix required diluting but she provided no further information as to why the analyst diluted only these two samples.

OBSERVATION (2). The reason for the dilution of samples 74A L01 and 74B L02 that resulted in non-detect status for sulfate should be fully resolved. It is unclear from the raw data why these samples could not be re-analyzed without dilution. One suggestion for preventing ND results would be to initially analyze all of the samples at a ratio of 1:5 instead of 1:10. It appears this dilution ratio would have resulted in detection of sulfate for these two samples without compromising the instrument.

**Microbial Insights, Rockford TN. Point of Contact: Michael Goodrich.
Sample Date 09/16/2002, Analysis Date 09/18/2002.**

Client Sample ID	Laboratory Sample ID
51A L01	A2919201
51B L01	A2919202
52A L01	A2919203
52B L01	A2919204
73A L01	A2919205
73B L01	A2919206
74A L01	A2919207
74B L01	A2919208

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Volatile Organic Acids, Microbial Insights, Point of Contact: Michael Goodrich. SOP No. VFA, Revision 1. (QAPP Table 6-4)

Raw QA/QC data were obtained for samples analyzed on September 18, 2002. The initial calibration and blank data met the requirements outlined in the QAPP, Table 6-4. The CCV and LCS standards are now run at 40 ppm and are within the method required limits. Matrix spike and matrix spike duplicate data met the project requirements for recovery, the relative percent difference was less than 20% for all six analytes. There appears to be a slight error in the reported value for propionic acid in sample 52B L01. The raw data indicates the correct value is 14 mg/L, the final STL-Buffalo report has a value of 16.9 mg/L. STL- Buffalo is reviewing the data to determine the correct value.

Sample reporting limits are 1 mg/L for all acids with the exception of pyruvic which is at 4 mg/L. Observation 2 is repeated in this report.

OBSERVATION (3): The project participants should decide if the reporting limits from Microbial Insights are sufficient and modify the QAPP as necessary.

Gas Samples:

Severn Trent Services- Los Angeles. STL Lot Number E2G020329 Amended and STL Lot Number E2F180191. Samples (E2G020329 Amended) Received 07/01/2002, Date Sampled: 06/28/2002. Samples (E2F180191) Received 06/17/2002, Date Sampled: 06/13/2002. Project Manager: Marisol Tabirara.

Four samples (E2F180191) were received June 17, 2002. Two additional gas samples (E2G020329) were received by STL-LA on July 1, 2002. The chain-of-custody and canister field data records indicate both sets of samples were received in good condition.

Table 3. Gas Analysis Results

Sample	CO ₂ (%)	CH ₄ (%)	N ₂ (%)	O ₂ (%)	NMOC (ppm-C)	Toluene* (ppb, TO-14)
51 G01	36	49	16	2.9	2000	13000
52 G01	20	25	49	11	1500	10000
73A G01	41	53	2.7	0.40	8300	46000
73A G02	41	53	1.8	ND (0.18)	11000	52000
73B G01	40	53	2.1	ND (0.18)	5300	51000
73B G02	46	55	ND (1.8)	ND (0.18)	5100	38000

Toluene concentration provided from TO-14 analysis as an indication of HAP levels .

Critical Measurements: (QAPP QA Objectives in Table 6-9)

Fixed Gases (Carbon Dioxide, Methane, Oxygen): Method 3C (QAPP Table 6-9).

Review of the data packages for Method 3C indicates the data met the QC requirements for accuracy and precision for the LCS and LCS duplicate. LCS samples had a recovery range of 106 to 111% for carbon dioxide (spike at 1%) and 106 and 112% for methane (spike at 0.0500%). Precision of the samples was well within the limit of 0-20%. The blanks were also found to be free from contamination.

Non-Critical Measurements:

Total Non-Methane Hydrocarbons: Method 25C Modified

Both data packages from Roger Green were reviewed and no QA/QC issues were found out of compliance. Method blank was ND at 30 ppm-c. Laboratory Control Samples had recoveries ranging from 108 to 100% recovery with the highest RPD of 2.3%. Spike amount was 600 ppm-c.

Hazardous Air Pollutants: Method TO-14A

Both data packages from Roger Green were reviewed and no QA/QC issues were found out of compliance. Method Blank was ND for all target analytes at low ppbv concentration. Laboratory Control Samples (50 ppb for 1,1-Dichloroethene, Methylene Chloride, Trichloroethene, Toluene and 1,1,2,2-Tetrachloroethane) had recoveries of 88-110% and RPD values of less than 6%, both QA indicators are within the limits specified in the QAPP.

**USEPA/Office of Research and Development
National Risk Management Research Laboratory**

Independent Data Validation

**Independent Data Validation of
Outer Loop Landfill Experimental Data**

**Performed by:
David A. Gratson
Neptune and Company**

Date of Report: 8/21/2003

Experimental Data: 3rd Quarter 2002, 1st & 2nd Quarters 2003

**Task No: 05 WO Seq. No. 07b
EPA Task Order Manager: Scott Jacobs**

Introduction: Data collection is in progress for the Landfill Bioreactor Studies at the Outer Loop Landfill, Louisville, Kentucky. These activities are guided by the Quality Assurance Project Plan, latest revision (Draft Final) dated May 6, 2003. The purpose of this task is to review and validate the data obtained in this project. To accomplish this, data were obtained from Roger Green, Waste Management Incorporated and from Morton Barlaz, NCSU during a Technical Systems Audit at his laboratory in August, 2003. The data packages from Roger Green included results from Severn Trent Laboratory - Buffalo (STL-Buffalo) for leachate and Severn Trent Laboratory- Los Angeles (STL-LA) for gas samples. The STL-Buffalo reports included analysis for Volatile Organic Acids that was subcontracted to Microbial Insights. This validation process reviewed all critical parameters and a few of the non-critical analyses included in the data packages and outlined in the QAPP Section 3.2, tables 3-4 to 3-6. The results of the data validation are outlined below and categorized by medium.

Data packages were evaluated (where appropriate) for Sample Identification (QAPP Section 4.7.1), Chain of Custody (QAPP Section 4.7.3), Correct Analytical Methods (QAPP Table 5.1), Container Preservation and Holding Times (Table 4-1), Detection/Reporting Limits (QAPP Table 6-9) and Laboratory Quality Control for Critical Measurements, QAPP Section 6.4 (Tables 6-2 to 6-9).

Limited amount of QC information is provided in the standard (Level II) data packages, however matrix and laboratory control spikes were included in the leachate data packages and QC requirements for the MSW data were reviewed in a recently completed audit.

Overall the results from data validation indicate most laboratory analyses are in compliance with the QAPP quality control requirements. **ALL CRITICAL DATA REVIEWED CAN BE USED** in project reports. Some data has been qualified due to quality control issues identified and should be used with caution. The use of the data is context specific. For example, Volatile Organic Acids with low spike recoveries may indicate negative bias. However, one might assume all samples had similar bias and are thus comparable. More caution may be in order when comparing samples for BOD where one or more were analyzed out of holding times.

Leachate Samples: STL-Buffalo

Critical Leachate Parameters: BOD, COD, Volatile Organic Acids (Microbial Insights). Some of the files also contained field data for pH (critical) and conductivity.

Eleven Acrobat (pdf) files were obtained from STL-Buffalo with results for leachate analysis. The files were associated with samples collected from November 2002 to July, 2003. Acrobat Files: A02-A447, A02-B373, A02-C503, A03-0709, A03-1405, A03-2498, A03-3377, A03-5054, A03-5431, A03-5975, A03-7170.

Excel spreadsheets (with the same name as the Acrobat files) with the summary data were also received and validated for data qualifiers.

QA Evaluation:

File A02-A447, samples 51A, 51B, 52A, 52B, 73A, 73B, 74A, 74B, sampled 10/21/02: The pH check (using a 7.0 buffer solution) reading was 7.28. The QC requirements for verification of pH are 7.00 ± 0.1 units (Table 6-1-1). These data are qualified as potentially biased high (J+) due to the results of this QC check. Butyric acid had low recovery (60.7 and 74.7%) in the matrix spike and duplicate. All samples were ND for butyric acid (1 mg/L limit), there is potential for false negative results due to this low recovery.

File A02-B373, samples 51A, 51B, 52A, 52B, 73A, 73B, 74A, 74B, sampled 11/14/2002: One set of samples (51A L01, 51B L01, 52A L01, 52B L01) was not preserved for COD when received (within 24 hours, good condition), the laboratory added sulfuric acid to achieve the required pH.

File A02-C503, samples 51A, 51B, 52A, 52B, 73A, 73B, 74A, 74B, sampled 12/16/2002: Acetic and propionic acid (Volatile Organic Acids) had very high matrix spike recoveries (300-400%). All samples (especially 74A L01, 74B L01) are qualified as potentially biased high (J+).

File A03-0709, samples 51A, 51B, 52A, 52B, 73A, 74A, 74B, sampled 1/22/03: 74A L01 BOD results were qualified by the laboratory as estimated (E) because the holding time was out of compliance (the initial dilution resulted in oxygen concentration that did not meet the method criteria). These BOD results should be used with caution.

File A03-1405, samples 51A, 51B, 52A, 52B, 73A, 73B, 74A, 74B, sampled 2/12/2003: All samples for COD/ammonia/total phosphate were received unpreserved. The laboratory added sulfuric acid to achieve the desired pH (within 24 hours of sampling). The initial BOD analysis for sample 73B L01 was depleted in oxygen; the reanalysis was performed out of holding times. Both results were reported, the first is qualified as estimated (72.0E), the second results was 74.7 mg/L. These BOD results should be used with caution.

File A03-3377, samples 51A, 51B, 52A, 52B, 73A, 73B, 74A, 74B, sampled 4/10/03: Samples 74A L01 and 74B L01 were received unpreserved. The laboratory added sulfuric acid to achieve the desired pH.

File A03-5054, samples 51A, 52A, 52B, 73A, 73B, 74A, 74B, sampled 5/23/2003: The initial BOD analysis for sample 74A L01 was depleted in oxygen; the reanalysis was out of holding times. Both results were reported (without qualification): ND (reporting limit 1800), reanalysis 216 mg/L. The reanalysis result should be qualified as estimated (E) and used with caution.

File A03-5431, samples 51A, 51B, 52A, 52B, 73A, 73B, sampled 6/5/2003: The pH check (using a 7.0 buffer solution) reading was 7.13. The samples are qualified as potentially biased high (J+) due to the results of this QC check. The RPD results for propionic and butyric acid are greater than the 20% limit; the LCS meet the QC requirements for all acids. Matrix spike recovery for pyruvic acid is low (56.8%, 54.7%). All samples were ND for pyruvic acid (4 mg/L limit), there is potential for false negative results due to this low recovery.

File A03-5975, samples 74A and 74B, sampled 7/14/2003: The matrix spike recovery for pyruvic acid was 51.8 and 52.0%. Pyruvic acid is ND in both samples, there is potential for false negative due to this low recovery.

File A03-7170, samples 51A, 51B, 52A, 52B, 73A, 73B, 74A, 74B, sampled 7/25/2003: The pH check (using a 7.0 buffer solution) reading was 7.16. The samples are qualified as potentially biased high (J+) due to the results of this QC check.

A number of sample reports indicated interference with the non-critical parameter nitrite. These data should be used with caution since bias is likely. All results with an estimated (E) qualifier from the laboratory (e.g. BOD) should be used with caution. BOD, in particular, is susceptible to degradation and negative bias if analysis is not started within 24 hours.

MSW Samples: NCSU

Critical MSW Parameters: Moisture, Organic (Volatile) Solids, BMP.
Excel Files: BMP_1_08_04_03, BMP_2_08_04_03, Lablogbook, LablandfillsMoistures, OL#3 data 081903, Volatiles-OL Set 3.

QA Evaluation:

Moisture and Organic (Volatile) Solids data was evaluated by reviewing the excel spreadsheets provided. The parameters are obtained by weighing samples before and after drying (65°C) or oxidation (550°C). Data validation is performed by ensuring the spreadsheets are correctly calculating the parameter using the entered data. This data is entered into the spreadsheet by the analysts and spot checked by peers, and/or Dr. Barlaz at NCSU. No problems were identified with the Moisture or Organic Solids data.

BMP data was evaluated from two spreadsheets that contain MSW samples from the November, 2002 sampling period. The spreadsheets contain daily calibration information along with the calculations for methane (corrected for STP and inoculum blanks), nitrogen, carbon dioxide, and oxygen. The precision (RSD/CV) is calculated for each set of triplicate samples (each sample undergoes the complete incubation and gas analysis process) and evaluated against the 20% criterion. Samples that exceed this criterion are re-analyzed (complete process) until the metric is achieved. A few minor mistakes in

formulas within the spreadsheet were noted and discussed with Dr. Barlaz. These errors have been corrected and a consistent model is now used to calculate methane. There are six sets of data in which the lowest calibration standard (10% methane) was unavailable. The SOP for calibration requires at least three calibration levels. However, after evaluating the calibration data I believe these data are valid. The slope of the calibration model for these six sets is very similar to that obtained using a full calibration. There is 3.1% difference in the average slope between the calibrations with three levels versus the calibration with two levels. This potential error level is within the precision of this analytical method. However, all future analyses should follow the method that requires at least three calibration levels*.

Gas Samples: STL-LA

Critical Parameters: Methane, Carbon Dioxide, Oxygen via Summa Canisters.
Acrobat Files: E2K250218, E12300222, E2L300223, E3D160263, E3F100284, M2C260265, E2F180191, E2G026329, M1C200280, M1L200214. Excel Files with the same names were also obtained, these contain summary data.

QA Evaluation:

The only quality issue noted for the critical parameters for the gas samples is holding times. A number of samples were analyzed between 7 and 14 days after collection. The QAPP specifies a holding time of 7 days (Table 4-1). There is no reason to believe the composition of the gas samples (methane, carbon dioxide, and oxygen) are compromised when analysis is performed within 14 days of collection (using Summa Canisters). For reference, Method 3C does not list a holding time and Method TO-14A has a 30 day holding time. All other QA/QC issues met the method and/or QAPP specifications.

* While evaluating the methane calibration data received with the BMP results two issues arose that could potentially improve the current method. These ideas came out of a meeting held with David Gratson and Vicki Lancaster of Neptune and Company, Inc. and Morton Barlaz. The current calibration method is acceptable; however improved calibration precision may be achieved through the use of a weighted least squares regression model. The idea of using a single calibration slope that is acquired on a single day, then verified during daily calibrations is also being considered. NCSU is currently performing additional calibration to test these ideas.